Nanofiltration of solutions containing organic and inorganic salts: Relationship between feed and permeate proportions

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A B S T R A C T

Nanofiltration can be considered for the purification of valuable products obtained by fermentation, like organic acids. In this work, nanofiltration experiments are carried out with synthetic solutions of different compositions containing acetate (Ac), propionate (Pr), and butyrate (Bu), as well as inorganic salts (NaCl). Although the retention of charged solutes can be significantly modified according to the composition of the solution, it is observed that there is a filtration flux above which the solutes proportions in the permeate remain constant. These proportions do not depend on the total concentration but only on the solutes proportions in the feed. Finally, individual solute transfer is found to vary linearly with the total solute flux. Similar trends are observed with two NF membranes despite their different properties.

1. Introduction

Nanofiltration (NF) is a pressure-driven membrane process used for liquid-phase separation. The retention mechanism in NF is a combination of different contributions, mainly due to the size (steric effect) and to the charge of the solutes and the membrane. NF is efficient for the recovery and selective removal of different kinds of products from complex solutions. Nowadays, NF is commonly used for various purposes, like water softening [1], brackish water desalination [2], wastewater treatment [3], whey demineralization [4], organic acid production [5] or drinking water production [6].

Volatile Fatty Acids (VFAs), also referred to as Short-Chain Fatty Acids (SCFAs), are organic acids having up to six carbon atoms [7]. They are recognized as promising chemical building blocks in the biorefinery concept [8]. There is a great interest in producing VFAs by fermentation of various biomass like household solid waste [9] or waste streams such as waste water [10] or waste activated sludge [11], with a double purpose of waste valorization and production of valuable compounds. Amongst VFAs, acetic, propionic, and butyric acids are the main components obtained in the fermentation broth.

Retention of ions contained in single electrolyte solutions was widely reported. The influence of ions size and charge was discussed [12], and a qualitative prediction of the retention sequence of ions with different valence and size was given [13]. Different models based on irreversible thermodynamics were proposed to describe the retention of single electrolyte solutions [14–16].

However, when more complex solutions are concerned, like multi-electrolytes systems, interactions between the different ions take place. Then, the retention of ions in mixed solutions cannot be predicted from the ones obtained with single solutions. An attempt to use an irreversible thermodynamic model to predict the individual ions' retentions in a Cd^{2+}/Ni^{2+} binary solution showed that the experimental retention of the less retained ion, Cd^{2+}, is 10% lower than that predicted by the model [17]. With binary systems containing two co-ions and only one counter-ion, it was reported that when one of the co-ions is totally retained by the membrane, the retention of the other decreases significantly. It was attributed to the co-ions competition. For instance, during NF of a mixture containing NaCl and an organic acid sodium salt, with a molecular weight (MW) of 700 g mol^{-1} and retention higher than 99%, negative retention of Cl^- was observed [18]. Same results, i.e. negative retention of the less retained ion, were also reported with ions of smaller molecular weight (lesser than 200 g mol^{-1}), especially for solutions containing co-ions with significant retention differences. As an example, negative retention of Cl^- was observed in the presence of SO_4^{2-} [19], and negative retention of Na^+ was reported in the presence of Ca^{2+} [20].

Such interactions of charged solutes in mixed solutions not only depend on operating conditions such as filtration flux but also on the feed composition, i.e. concentration and proportions of ions. It was reported that, for a mixed solution containing NaCl and an organic acid sodium salt, the retention of Cl^- decreases to more negative values when

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the proportion of organic acid salt in the feed increases [18]. This was also observed with solutions containing Na_2SO_4 and $NaNO_3$, for which negative values are obtained for the retention of NO_3^- when the concentration ratio of SO_4^{2-} /NO_3^- in the feed increases from 1 to 5. Again, more negative values are observed for an increasing concentration ratio up to 10 [21]. Negative retentions of acetate were also reported during NF of a succinate/acetate binary solution for certain feed compositions, i.e. for a concentration about 0.7 M and an acetate/succinate ratio of 6, while both acetate and succinate retentions are positive for lower concentrations or lower acetate/succinate ratio [22]. More complex mixtures containing formate, acetate, lactate, and succinate salts were investigated too. It was found that the retentions of the less retained solutes, lactate, acetate, and formate, decrease in the presence of succinate, a more retained solute and that this decrease is more important for increasing proportion of succinate [23]. The mechanisms involved in co-ions interactions, such as steric effect and dielectric effect, are discussed in a comprehensive paper on negative retention [24].

This work reports an experimental study dealing with nanofiltration of solutions containing VFAs salts at pH 8, for which VFAs are totally dissociated. Solutions of increasing complexity are used from single VFA solutions (acetate, propionate, and butyrate) at different concentrations to binary and ternary mixtures of VFAs of different compositions. Addition of NaCl is also investigated. The influence of the feed composition on the individual solutes retentions is first discussed. Then, additional parameters are investigated, like the solute proportion in the permeate and the solute transfer. Some results obtained with another membrane are reported in order to assess the genericity of the conclusions.

2. Materials and methods

2.1. Nanofiltration membranes and chemicals

Two types of flat sheet composite membranes, NF 45 and XLE membranes (Filmtec, Dow), were used in this work, the main characteristics of which are provided in Table 1. The pH of the solutions was between 8 and 9, so both the membranes and the VFAs were negatively charged. The synthetic solutions of VFA were prepared using sodium acetate, sodium propionate, sodium butyrate (provided by Acros organics, with more than 99% of purity), and sodium chloride, dissolved in ultra-pure water. Table 2 shows the characteristics of the VFAs in neutral forms. The feed compositions of single, binary and ternary solutions of VFAs, as well as the solutions of VFAs + NaCl, are summarized in Table 3. Several total concentrations were investigated (from 100 mM to 500 mM).

2.2. Analytical methods

The concentrations of acetate, propionate and butyrate in single solutions were measured by a refractometer (ATAGO AX500, USA). VFAs concentrations in mixed solutions were obtained by High-Performance Liquid Chromatography (HPLC) (Jasco LC Net II/ADC, Japan) equipped with a Shodex SH1011 (Showa Denko, Japan) column and a UV detector (wavelength was set at 280 nm). The column temperature was set at 50 °C, and 10 mM sulfuric acid was used as the mobile phase at a flow rate of 1 mL min^{-1}. The injection volume was 10 µl, and the samples were diluted with ultra-pure water to be in the concentration range from 5 mM to 50 mM. With this method, the limit of quantitation for VFAs is lower than 0.1 mM. The concentrations of NaCl were measured by ion chromatography. Ion chromatography system (ICS-3000, Dionex, France) was using an IonPac™ AS11 column, equipped with an auto sampler AS50 and conductivity detector CD20. The injection volume was 25 µL and the temperature was set at 30 °C. Samples were diluted to a maximum of 1000-folds by ultra-pure water before analysis.

Table 2
Characteristics of the VFAs.

Name	Acetic acid	Propionic acid	Butyric acid
Structure			
Molecular weight (g.mol^{-1})	60.05	74.08	88.11
pK_a (25°C)	4.76	4.88	4.82

2.3. Experimental procedure

NF experiments were carried out using a dead-end stirred filtration cell. The total volume of the cell was 400 mL. The stirring speed was set at 108 rpm. A piece of NF-45 or XLE membrane was placed at the bottom of the cell, supported by a 316 L stainless steel porous disc. The active membrane surface was 30 cm^2. Pressurized air was used to pressurize the cell. The pressure was controlled manually by a valve. Filtration was operated at room temperature (between 20 and 27 °C). Permeate was timed and measured by an electronic balance to calculate the filtration flux.

Membrane conditioning and cleaning procedures are crucial to obtain accurate data. The membrane was first immersed in ultra-pure water for 24 h. It was then compacted by filtering ultra-pure water at a pressure of 20 bar until the filtration flux, J reaches a constant value. The linearity of J versus ΔP was checked and the water permeability L_{p0} was calculated by the slope of $J/\Delta P$. After each NF experiment, the membrane was washed twice by filtering 200 mL of ultra-pure water and the water permeability was measured to check any membrane fouling or aging.

In addition to pure water permeability, retention of glucose (molecular weight: 180 g mol^{-1}) was measured regularly to detect any membrane modification during the experiments. One piece of NF-45 membrane and one piece of XLE membrane were used in this work. The pure water permeability increased from 1.6×10^{-6} m s^{-1} bar^{-1} and 1.5×10^{-6} m s^{-1} bar^{-1} at the beginning to 2.0×10^{-6} m s^{-1} bar^{-1} and 1.9×10^{-6} m s^{-1} bar^{-1} at the end of the experiments, for NF-45 and XLE membranes respectively. The increase of the pure water permeability during multiple experiments is usually observed, such as reported for Desal-5 DK membrane [30]. This phenomenon could be due to the "aging" of the membrane, the mechanism of which was not yet elucidated. Meanwhile, the retention of glucose by the two membranes remained almost constant, about 92% for NF-45 membrane, and higher than 99.5% for XLE membrane at a transmembrane pressure of 20 bar, during the entire period of experimentation.

For each experiment, 400 mL of solution was initially fed into the cell. Then, the pressure was increased step by step (4, 8, 12, 16, 20 bar). For each pressure investigated, the filtration flux was measured after reaching a steady-state, and 1.5–2 ml of permeate was then collected for

Table 1
Characteristics of NF-45 and XLE, Dow Filmtec membranes.

Membrane	**MWCO (g. mol^{-1})**	**Active layer material**	Maximum temperature (°C)	Max. pressure (bar)	pH range	Membrane isoelectric point	**Pure water permeability (m·s^{-1}·bar^{-1}, 25°C)**
NF-45	200	Polyamide	45°C	41 [25]	2–12	4 [26]	1.57×10^{-6} [27]
XLE	100	Polyamide	45°C	41	2–11	4 [28]	2.16×10^{-6} [29]

Table 3
Compositions of the synthetic solutions for three total concentrations, 100 mM, 200 mM and 500 mM.

solutes	Single solutions (%)				VFAs mixed solutions (%)									VFAs + NaCl (%)[b]					
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10[a]	S11	S12	S13	S14	S15	S16	S17	S18	S19
Acetate	100				50	20		50	20	33	60	20	20	25	20	10	17	13	7
Propionate		100			50	80	50			33	20	60	20				17	13	7
Butyrate			100				50	50	80	33	20	20	60	25	20	10	17	13	7
NaCl				100										50	60	80	50	60	80

[a] For S10, proportion of Ac:Pr:Bu = 33%:33%:33%, two additional total concentrations were also used (300 mM, 400 mM).
[b] For the synthetic solutions of VFAs + NaCl, the total concentrations of S14 and S17 are 200 mM, S15, S16, S18, and S19 are 500 mM.

analysis. For each experiment, approximately 60 mL of permeate was collected in total. It means that in the worst case, the concentration factor would be equal to 1.15.

For each experiment, the feed volume, V_f, permeate volume, V_p , and retentate volumeV_r, were determined, as well as the concentrations of the feedC_f, permeate, C_p , and retentate, C_r, using the previously detailed analytical methods. The mass balance, $V_fC_f = V_pC_p + V_rC_r$, was checked, and it was observed that the maximum difference does not exceed 5%.

As mentioned before, during the experiments, 60 mL of permeate was collected, so that the concentration in the retentate increased. Then, the retention calculated using the initial feed concentration is underestimated. However, it was checked that this underestimation does not exceed 3% and does not change the trends that will be discussed.

The experiments are repeated twice for VFAs single solutions at 100 mM and 500 mM, and the results obtained from the two filtrations can be fitted with one single curve.

2.4. Data treatment

The filtration flux, J, was calculated by Eq. (2.1):

$$J = \frac{V_p}{S_m \times t} \tag{2.1}$$

with the volume of permeate V_p (m^3), obtained by the weight of permeate; S_m the active surface of the NF membrane (m^2) and the unit of time, t in second (s).

The retention if solute i, R_i, was calculated from Eq. (2.2):

$$R_i(\%) = \left(1 - \frac{c_i^p}{c_i^f}\right) \cdot 100\% \tag{2.2}$$

The retention versus filtration flux curves were fitted using a simple model with two parameters proposed by Timmer et al. [16]:

$$R_i = \frac{A \times J}{J + B} \tag{2.3}$$

The proportion of individual solute i in the feed and permeate were calculated from Eqs. (2.4) and (2).5), respectively:

$$P_i^f = \frac{c_i^f}{c_s^f} = \frac{c_i^f}{\sum_{i=1}^{n} c_i^f} \tag{2.4}$$

$$P_i^p = \frac{c_i^p}{c_s^p} = \frac{c_i^p}{\sum_{i=1}^{n} c_i^p} \tag{2.5}$$

c_i^f concentrations of solutes i in the feed (mM)
c_i^p concentrations of solutes i in the permeate (mM)
c_s^f total solute concentration in the feed (mM)
c_s^p total solute concentration in the permeate (mM)
P_i^f proportions of solutes i in the feed
P_i^p proportions of solutes i in the permeate

The individual solute flux J_i, is defined as Eq. (2.6).

$$J_i = Jc_i^p \tag{2.6}$$

The total solute flux, J_s, is the sum of all the solute flux in the mixture, shown in Eq. (2.7).

$$J_s = Jc_s^p = \sum J_i = \sum (Jc_i^p) \tag{2.7}$$

Then, Eq. (2.5) can be rewritten as Eq. (2.8).

$$P_i^p = \frac{c_i^p}{c_s^p} = \frac{c_i^p}{\sum (c_i^p)} = \frac{Jc_i^p}{\sum (Jc_i^p)} = \frac{J_i}{J_s} \tag{2.8}$$

Therefore, the proportion of solute i in the permeate also represents the contribution of solute i to the total solute transfer.

3. Results and discussions

The experiments are carried out with two NF membranes and synthetic solutions from single VFAs solutions, mixed VFAs solutions, to mixed VFAs solutions with the addition of inorganic salt (NaCl). NF 45 membrane is used for a complete experimental investigation. Then, XLE membrane is also tested with a few conditions, to check if the trends pointed out with NF 45 membrane can be also applied to other membranes.

3.1. Nanofiltration with NF-45 membrane

3.1.1. Solutes retentions in single and mixed solutions

3.1.1.1. Single solutions. Retentions of solutes in single solutions (S1–S4) as a function of filtration flux are represented in Fig. 1a for the different concentrations. One can observe that for any solute, the retention increases with the filtration flux. Moreover, the retentions of the individual solutes continuously decrease for increasing concentrations. The retentions of individual solutes at various concentrations are further compared at a given filtration flux of 2×10^{-6} m s^{-1} (7.2 L m^{-2} h^{-1}) in Fig. 1b. One can observe that the retention of acetate (Ac) decreases from 65% to 38% as its concentration increases from 100 mM to 500 mM, with an intermediate value of 59% at 200 mM. The same tendencies are obtained for propionate (Pr) (72%, 68%, and 45%), butyrate (Bu) (88%, 73%, and 55%), and Cl (17%, 11%, and 5%) when the concentration increases from 100 mM, 200 mM, to 500 mM.

At pH 8, both Cl and VFAs are in their dissociated form and negatively charged (see pK_a values in Table 2). As previously mentioned, it is known that the retention of charged solutes depends on the combination of steric (size) effect and electrostatic interactions between the charged solutes and the membrane charge. The higher retentions observed at low concentrations are mainly due to electrostatic repulsions since both solutes and membrane are negatively charged at pH 8. Then, increasing concentrations result in lower retentions due to the screening effect, i.e. the decrease of electrostatic repulsions between the solutes and the membrane [31,32].

On the other hand, for any condition, one can observe that the retentions of solutes follow the sequence Cl < Ac < Pr < Bu, in agreement

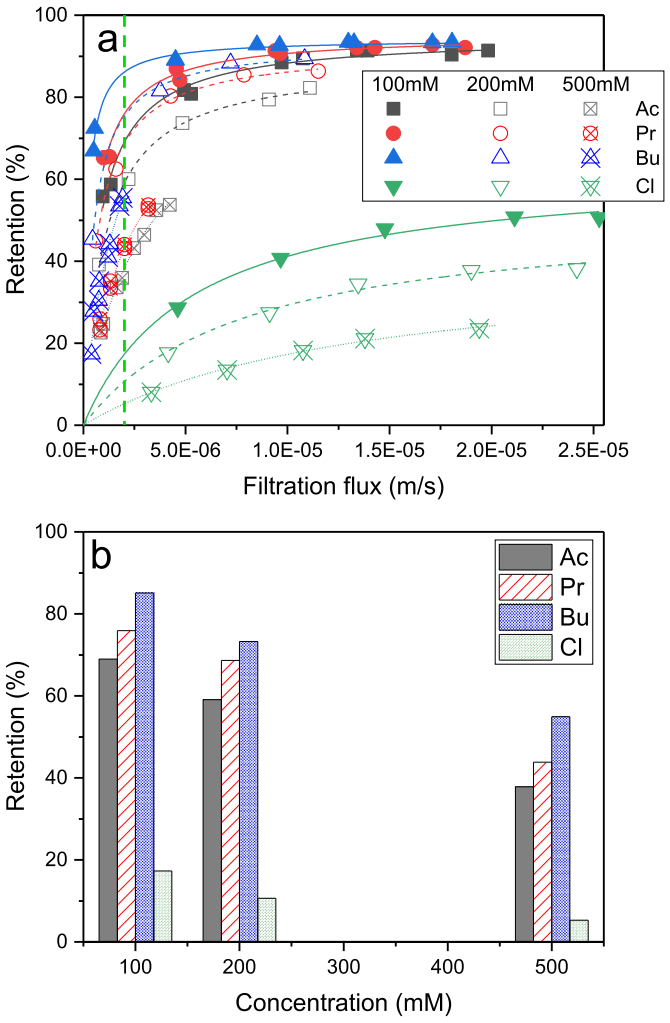

Fig. 1. Retention of VFAs and Cl in single solutions for different concentrations using NF-45 membrane. (a) retention versus filtration flux at different concentrations, (b) retention versus concentration at a filtration flux of 2×10^{-6} m s^{-1}.

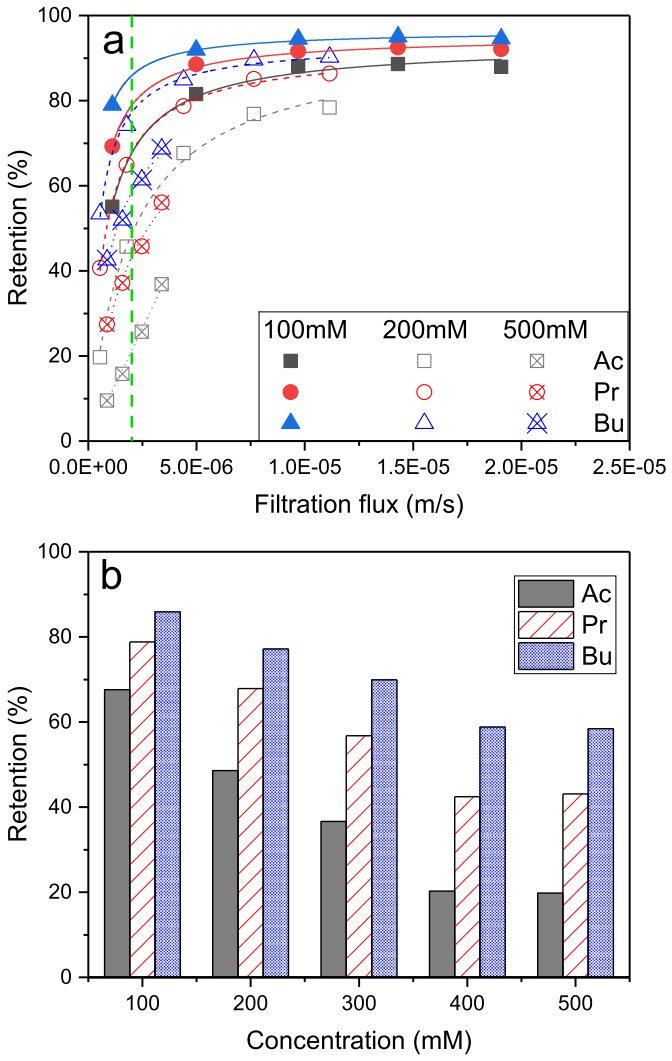

Fig. 2. Individual VFAs retention in ternary (Ac: Pr: Bu = 33%:33%:33%) solutions using NF-45 membrane. (a) retention versus filtration flux at different concentrations, (b) retention versus concentration at a filtration flux of 2×10^{-6} m s^{-1}.

with their molecular weights (Cl, 35.5 g mol^{-1}, Ac, acetate, 59 g mol^{-1}, Pr, propionate, 73 g mol^{-1} and Bu, butyrate, 87 g mol^{-1}). Comparable result was previously reported with other carboxylic acid salts at the same concentration (100 mM) with the following sequence for the solutes retentions: formate (45 g mol^{-1}) < acetate (59 g mol^{-1}) < lactate (89 g mol^{-1}) [23].

3.1.1.2. VFAs mixed solutions. Ternary solutions containing equal proportions of VFAs are firstly investigated.

The retentions of individual solutes in a ternary solution (S10, Ac: Pr: Bu = 33%: 33%: 33%) are plotted in Fig. 2a versus filtration flux for increasing total concentrations. As observed with single solutions, the solutes' retentions increase with the filtration flux. Fig. 2b shows the individual solutes retentions for different concentrations at a filtration flux of 2×10^{-6} m s^{-1}. Retentions of Ac, Pr and Bu decrease respectively from 68%, 79%, and 86%, for a total concentration of 100 mM, 49%, 68%, and 77%, at 200 mM, to 24%, 43%, and 58% for a total concentration of 500 mM. As previously mentioned for single solutions, the influence of the total concentration on individual solutes retentions is due to the screening effect. Then, as already observed with single solutions, the retention sequence is Ac < Pr < Bu for any total concentration. Moreover, the retention differences between Ac/Pr and Pr/Bu increase with the total concentration. The same trends are observed for binary solutions and ternary solutions with different concentrations and proportions (results not shown).

Fig. 3 shows the individual VFAs retentions at a given filtration flux in binary and ternary solutions with different proportions of VFAs, at a total concentration of 500 mM. The retentions in single solutions at the same concentration are given for comparison. It shows that the retention of the less retained solute decreases and that of the more retained one increases compared to those observed in single solutions (except for the retention of Pr in the binary solution with the proportion of Ac: Pr = 20%: 80%). In addition, the retention decrease of the less retained solute (Ac) is larger than the retention increase of the more retained solutes (Pr and Bu).

For binary solutions, Ac/Pr and Ac/Bu, one can observe that when the proportion of the less retained solute (Ac) decreases from 50% to 20%, the retentions of both VFAs decrease. This decrease is more pronounced for the binary solution of Ac/Pr than for that of Ac/Bu (Fig. 3a). For ternary mixtures, no clear trend is observed for the retentions of individual VFAs obtained with mixtures of different proportions (Fig. 3b).

For easier comparison of the individual solutes retention in single and mixed solutions, the retention difference, $(R_{mix}^{VFA} - R_{sgl}^{VFA})$, is plotted versus the filtration flux for all the conditions investigated (Fig. 4).

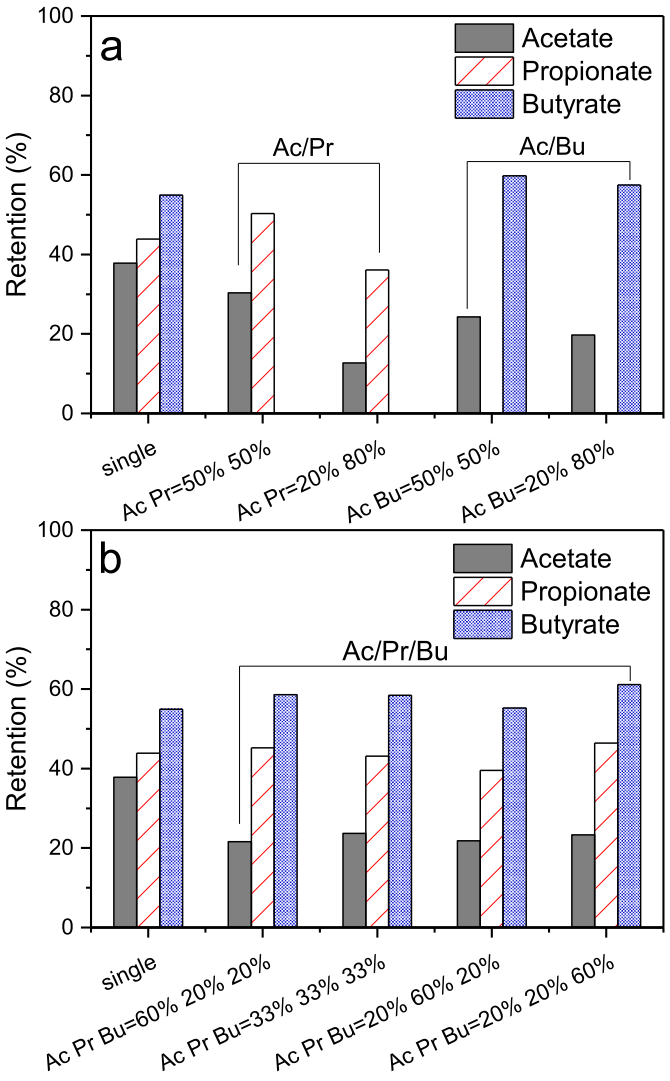

Fig. 3. Comparison of individual VFAs retentions in single and mixed solutions with different proportions at a filtration flux of 2×10^{-6} m s^{-1} and the total concentration of 500 mM using NF-45 membrane. (a) Binary solutions, (b) Ternary solutions.

Firstly, one can observe that the retention difference between individual VFAs in mixed and single solutions decreases when the filtration flux increases. Then, with a few exceptions, Fig. 6 shows that the retention of the less retained solute (Ac) is lower in the mixture compared to single solution while the retention of the more retained solute (Bu) is higher than in single solution. Furthermore, the retention difference is the highest for the highest concentrations and lowest fluxes. For Pr, its retention is between those of Ac and Bu and it can be either higher or lower compared with that in single solutions. No clear trend regarding the influence of the composition can be drawn.

3.1.1.3. VFAs mixed solutions with the addition of NaCl. Experiments are carried out with binary solutions of Ac/Bu, and ternary solutions of Ac/Pr/Bu with the addition of NaCl at different total concentrations, with different ratio of VFAs: NaCl in the feed solution (S14~S19).

Fig. 5 shows the retentions of all the anions in binary solutions of Ac/Bu and ternary solutions of Ac/Pr/Bu with the addition of NaCl. Retentions in single solutions of Ac, Pr, Bu, and Cl at the corresponding concentrations are given as references.

One can observe that the retention sequence in the mixed solutions is always Cl < Ac < Pr < Bu, the same as that in single solutions, for all the

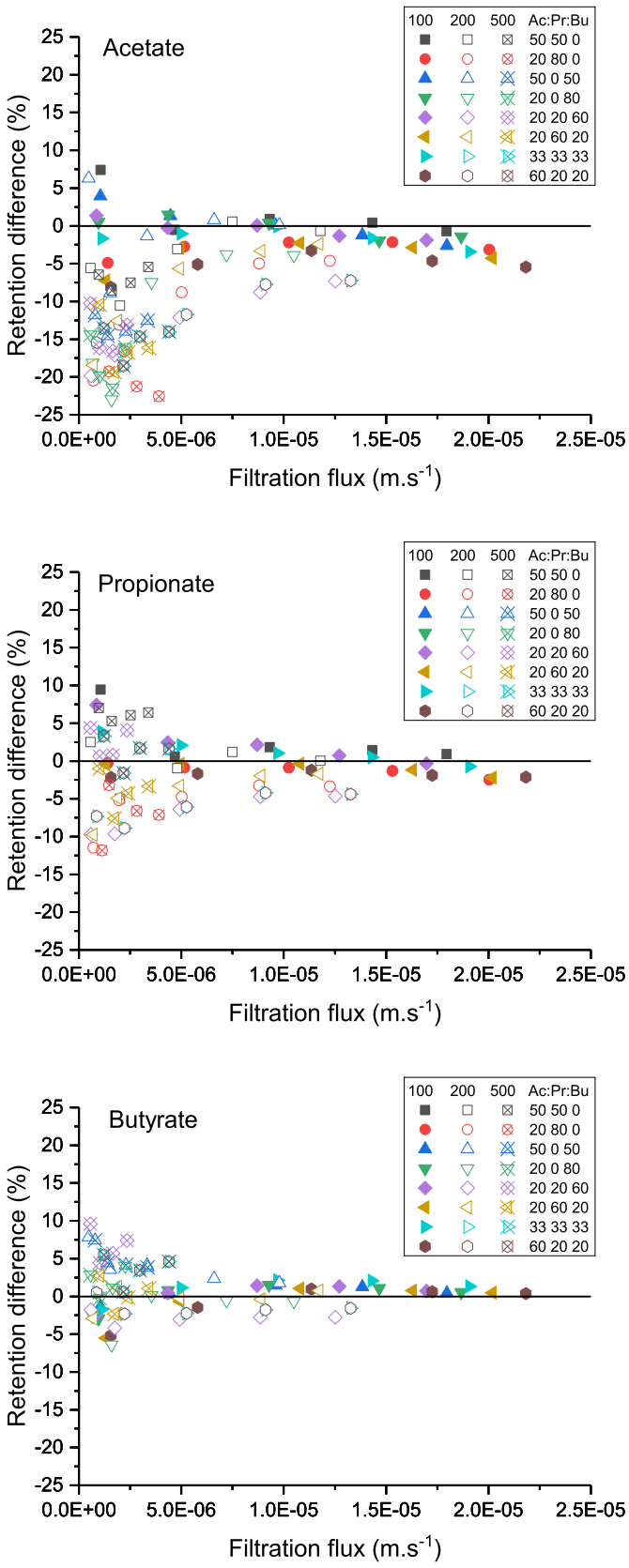

Fig. 4. Comparison of individual VFAs retentions in mixtures and single solutions- Retention difference ($R_{mix}^{VFA} - R_{sgl}^{VFA}$) versus filtration flux for all the conditions investigated using NF-45 membrane.

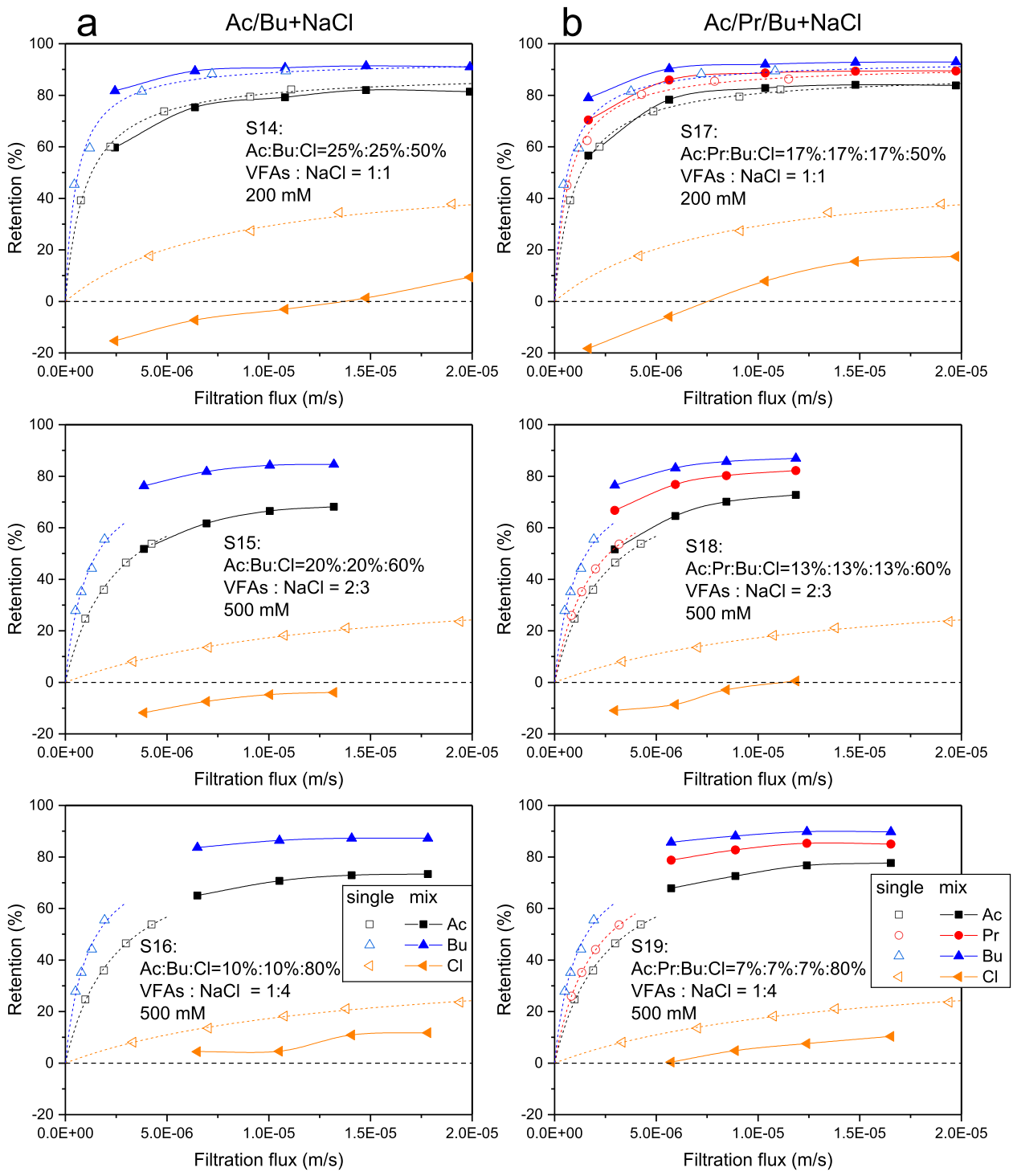

Fig. 5. Retentions of individual anions in single (empty symbols and dashed lines) and mixed solutions (full symbols and solid lines) versus filtration flux at different compositions using NF-45 membrane. (a) Ac/Bu binary solutions with NaCl, (b) Ac/Pr/Bu ternary solutions with NaCl.

compositions investigated.

Regarding VFAs, comparison of single and mixed solution is possible for the composition VFAs: salts = 1 : 1 at 200 mM. Slightly higher retentions are observed for butyrate in mixed solution compared to single one while no significant difference can be observed for Ac and Pr. For the other compositions, it is very difficult to compare because there is no common range of filtration flux between single and mixed solutions.

The retentions of Cl, the less retained solute, are much lower in the mixtures compared to single solutions and negative values are obtained for some conditions. The decrease of Cl retention in the mixture is related to the ratio between VFAs and Cl. Indeed, when the ratio between VFAs and Cl decreases from 1:1, 2:3, to 1:4, the decrease of Cl retention becomes less and less pronounced.

In Ac/Pr/Bu/Cl solutions, Cl is the less retained anion and Bu is the most retained one. Consequently, according to previous results, retentions of Cl and butyrate in mixed solutions are expected to be respectively lower and higher than those in single solutions. This is what is observed, with a more pronounced effect for Cl compared to butyrate, owing to the high retention of butyrate.

Then, a general trend is concluded, that is, in a mixed solution, the

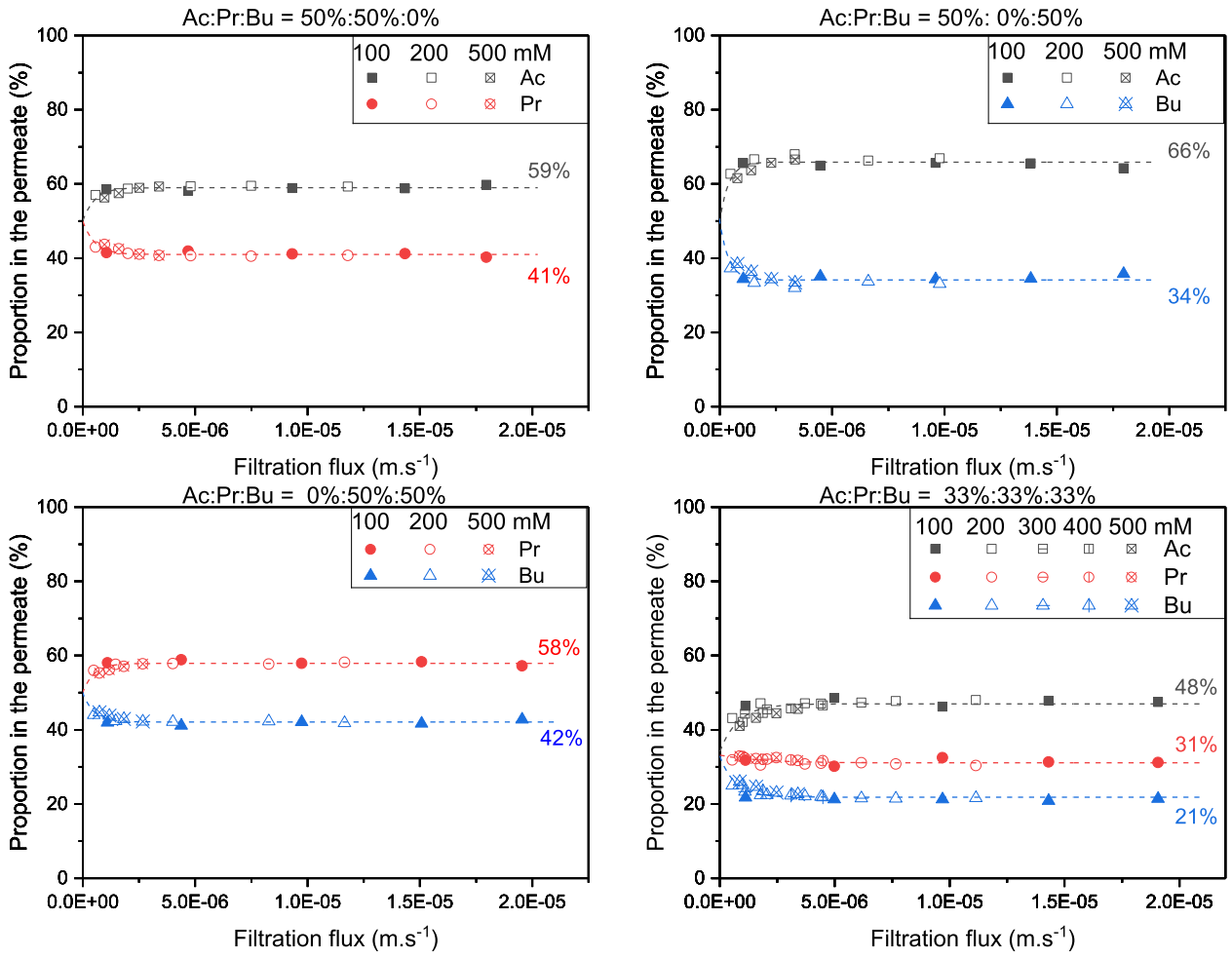

Fig. 6. Individual VFAs proportions in the permeate versus filtration flux for Binary (Ac/Pr, Ac/Bu, Pr/Bu) and ternary (Ac/Pr/Bu) solutions at different concentrations with identical VFAs proportion in the feed, using NF-45 membrane.

retention of the less retained solute decreases while that of the more retained one increases compared to single solutions. However, it is difficult to discern a trend regarding the influence of the proportions of solutes.

The current results are in agreement with previous ones. Indeed, for solutions containing monovalent and divalent organic acid salts of various molecular weights (formate, acetate, lactate, and succinate) it was also reported that the retention of the most retained solute, succinate, was higher in the binary mixtures than in the single solutions. Meanwhile, the retentions of the less retained acid salts, formate, acetate, and lactate, decreased significantly in the presence of succinate and even reached negative values under certain conditions. The extent of decline of monovalent acid salt retentions followed the sequence: formate > acetate > lactate [23]. This trend, i.e. increase of the retention of the more retained solute and decrease of the less retained solute, was mentioned as "distribution effect" [23] or "co-ions competition" [33,34]. The mechanisms involved in co-ions interactions were comprehensively discussed via investigation of the negative retention phenomenon [24]. For a system with one counter-ion and two co-ions of different mobilities, the electrokinetic charge density is zero. The more mobile co-ions are electrostatically attracted to the membrane phase to compensate for the potential deviations from electric neutrality arising due to the strong exclusion of the less mobile co-ions. Therefore, a decrease in the retention of more mobile co-ions is observed. This phenomenon is a general feature for mixed solutions with less and more retained ions using charged or uncharged membranes [24].The concentration ratio between the ions was suggested as one of the major factors influencing the retention decrease of the less retained solute [22, 31]. It was reported that the increase of the concentration ratio between the more and less retained co-ions makes the retention of the less retained co-ion decreasing [21–23,32,35]. For instance, during nanofiltration of a mixed solution of Na_2SO_4 and $NaNO_3$, a decrease of the NO_3^- retention was observed for an increasing concentration ratio of SO_4^{2-}/NO_3^- in the feed [21]. A decrease of acetate retention for increasing succinate/acetate ratio was also observed for mixtures of acetate and succinate [22]. However, on the contrary to our present study, different total concentrations were used for the different compositions, so that it was not possible to exclude an influence from the screening effect due to the increase in the total concentration.

3.1.2. *Solute transfer*

Besides retention, additional parameters, like solutes proportions in the permeate and solute fluxes are also considered in the present work. Fig. 6 shows the variation of individual VFAs proportions in the permeate versus filtration flux, for binary and ternary solutions with identical proportions of VFAs at different concentrations.

For all the conditions investigated, one can observe that the proportion of the less retained solute in the permeate increases when the filtration flux increases, and reaches a plateau (namely, $P_i^{p^*}$) when the filtration flux is higher than a certain value. This is the case for Ac in Ac/Pr, Ac/Bu, and Ac/Pr/Bu mixtures and for Pr in Pr/Bu mixture. At the same time, the proportion of the more retained solute decreases as the filtration flux increases, before reaching a plateau value. This is the case for Pr in Ac/Pr mixture and Bu in Ac/Bu, Pr/Bu, and Ac/Pr/Bu mixtures.

For the ternary mixture Ac/Pr/Bu, the proportion of Pr, which has a retention between the ones of Ac and Bu, decreases slightly compared to that in the feed (from 33% to 31%).

The same tendencies are observed for all the conditions investigated (S5–S13, listed in Table 3, results not shown).

For VFAs mixed solutions with the addition of NaCl, the solutes proportions in the permeate are given versus filtration flux in Fig. 7. It is shown that the proportion of Cl in the permeate increases when the filtration flux increases. Meanwhile, the proportions of VFAs decrease when the filtration flux increases. For all those anions, the proportion in the permeate reaches a plateau ($P_i^{p^*}$) when the filtration flux is higher than a given value. For VFAs, the permeate proportion of the least retained VFA, Ac, decreases the least, followed by Pr, the intermediately retained VFA, and the most retained VFA, Bu, decreases the most.

What is remarkable is that the permeate proportions (plateau values) obtained for same feed proportions but different total concentrations are identical (Fig. 6).

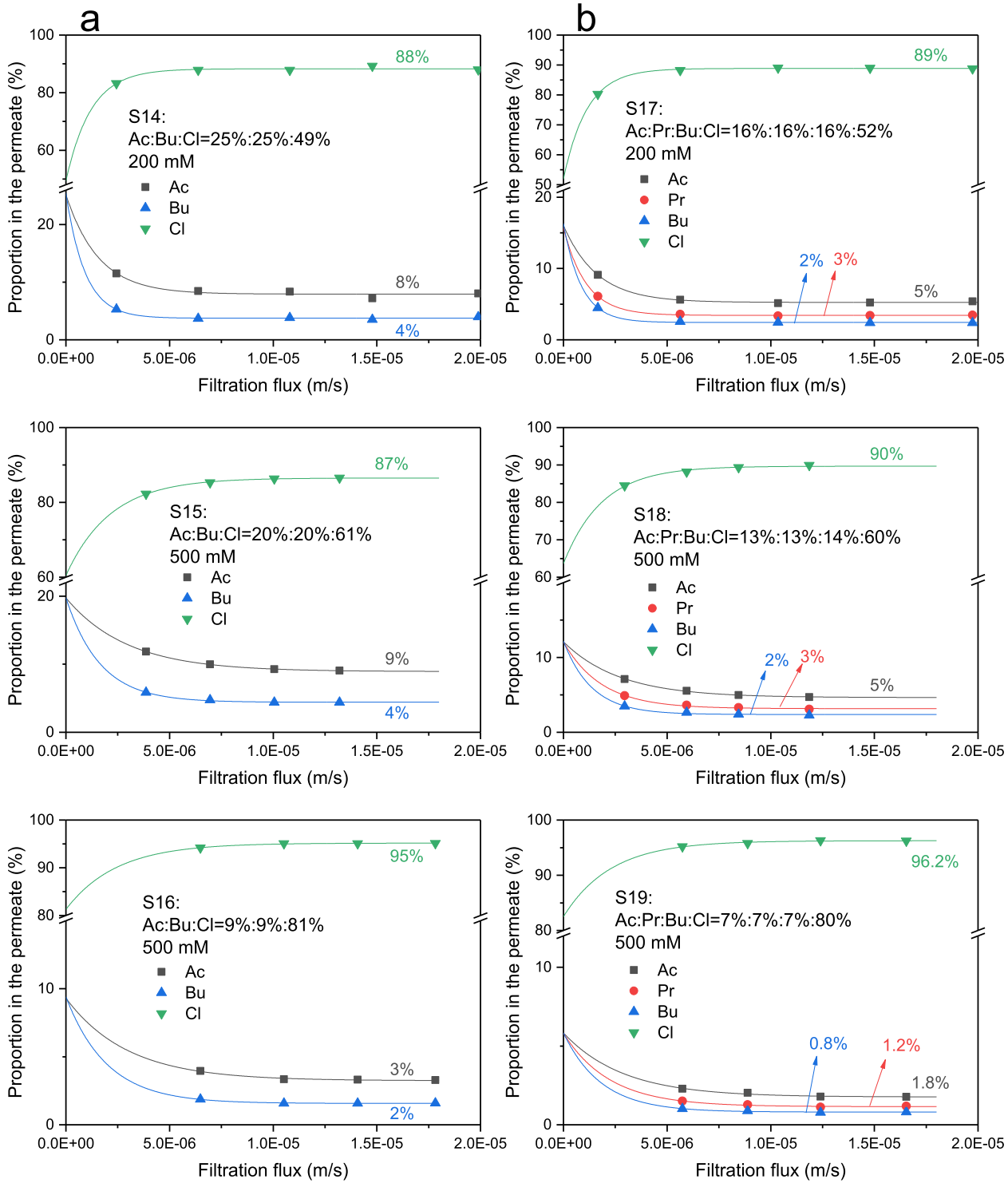

Fig. 7. Proportions of all the solutes in the permeate versus filtration flux, for (a) Ac/Bu binary solution with NaCl, (b) Ac/Pr/Bu ternary solution with NaCl, using NF-45 membrane.

Fig. 8 shows the individual solute flux versus total solute flux, for ternary solutions (Ac/Pr/Bu) without and with the addition of NaCl at different concentrations with identical proportions of VFAs. One can state that for any solute the individual solute flux increases with the total solute flux and that this variation is linear. Such a linear variation is also observed for all the conditions investigated (results not shown). Moreover, it does not depend of the total concentration.

According to Eq. (2.8), the slope of the straight giving the variation of individual solute flux versus total solute flux represents the contribution of the given solute to the total solute transfer, that is the proportion of the given solute in the permeate. Indeed, the values obtained for the slopes of the linear fitting are in very good agreement with those obtained for the constant proportions (plateau values of the variation of proportions in the permeate versus filtration flux) previously reported.

The proportion in the feed and in the permeate (plateau values of proportion versus filtration flux, $P_i^{p^*}$) are given in Table 4 for all the conditions investigated.

To easier the study of the influence of feed proportions on permeate proportions, ternary plots are used to visualize the results and see if a general trend can be drawn.

Fig. 9 shows the ternary contour graphs of the VFAs proportions in the permeates of single and mixed solutions for all the proportions investigated. Those plots use the proportion of Ac, Pr, and Bu in the feed as three coordinates (from 0% to 100%), and color from dark blue to deep red to represent the proportion of corresponding VFA in the permeate from 0 to 1 (with contour lines at 0.20, 0.40, 0.60, and 0.80 indicated). The dashed contour lines represent the constant feed proportion of the given VFA, while the full contour lines represent the constant permeate proportion of the given VFA.

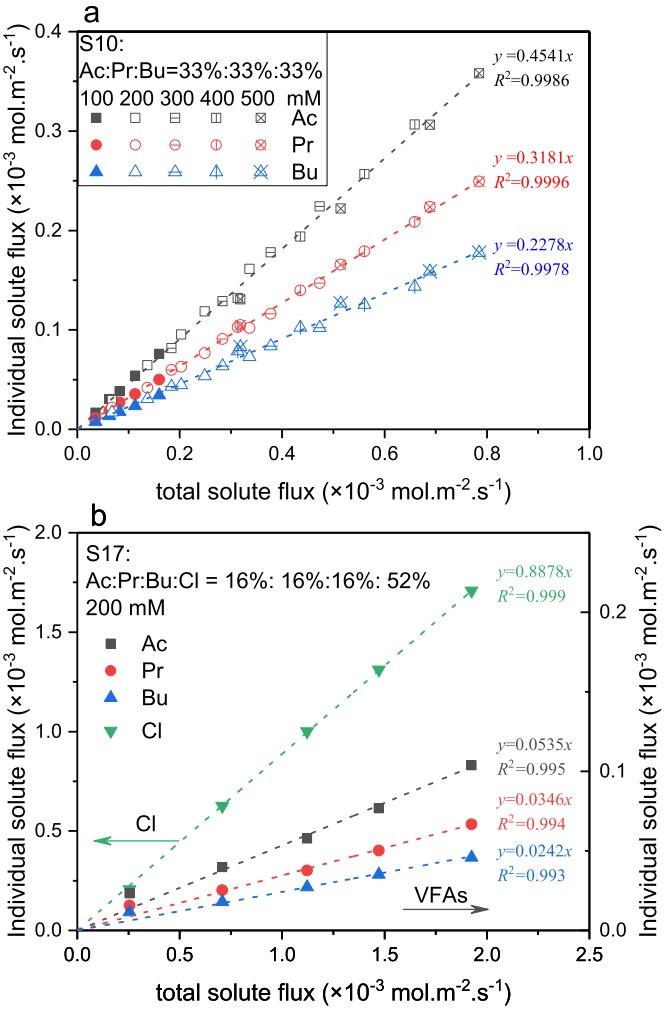

Fig. 8. Individual solute flux as a function of total solute flux, for ternary (Ac/Pr/Bu) VFAs solutions at different concentrations with equal proportions of VFAs (33% or 16%), for (a) VFAs solutions, (b) VFAs + NaCl solution, using NF-45 membrane.

Table 4

VFAs proportions in the feed (P_i^f) and permeate (plateau values of proportion versus filtration flux, $P_i^{p^*}$) for all the conditions investigated, using NF-45 membrane.

Solution	Feed proportion (P_i^f)			Permeate proportion ($P_i^{p^*}$)		
	Ac	Pr	Bu	Ac	Pr	Bu
S1	1.00			1.00		
S2		1.00			1.00	
S3			1.00			1.00
S5	0.50	0.50		0.59	0.41	
S6	0.20	0.80		0.25	0.75	
S7		0.50	0.50		0.58	0.42
S8	0.50		0.50	0.66		0.34
S9	0.20		0.80	0.32		0.68
S10	0.33	0.33	0.33	0.47	0.31	0.22
S11	0.60	0.20	0.20	0.72	0.16	0.11
S12	0.20	0.60	0.20	0.27	0.59	0.14
S13	0.20	0.20	0.60	0.31	0.21	0.48

One can firstly observe that, the proportions of VFAs in the permeate continuously change when the proportions of VFAs in the feed gradually change. This indicates that there is a direct link between the proportions of VFAs in the feed and permeate.

For Ac, it is observed that the dashed contour lines (representing the Ac proportion in the feed) are always lower than the full contour lines (represent the Ac proportion in the permeate). This indicates that the proportion of Ac in the permeate is always higher than the proportion of Ac in the feed. Moreover, the full and dashed contour lines are not parallel, show the influence of the proportions of those two VFAs. Indeed, the more difference between the full and dashed line are observed on Ac axis, indicate that when the ratio of Bu/Pr increase, the proportion of Ac in the permeate increases.

For Bu, dashed contour lines (representing the Bu proportion in the feed) are always higher than the full contour lines (represent the Bu proportion in the permeate). This indicates that the proportion of Bu in the permeate is always lower than that in the feed. Again, the full and dashed contour lines are not parallel, with more difference at the Ac axis, indicate that when the ratio of Ac/Pr increases, the proportion of Bu in the permeate decreases.

However, for Pr, dashed and full contour lines crossover each other, the conditions those two lines cross each other can be fitted with a straight line (i.e. the purple dashed line). This indicates that the proportion of Pr in the permeate is lower than that in the feed on the right side of the triangle, while it is higher than that in the feed on the left side of the triangle. The conditions for which the proportions of Pr in the permeate equal to those in the feed are on the purple dashed line, which is when the ratio of Ac: Bu = 2:3 (or 40%:60%).

Considering the retentions of individual solutes, the trend concerning different feed proportions is not clear. However, considering the permeate proportion (i.e. the distribution of the total solute flux between the solutes), a clear tendency is observed, as discussed previously.

3.2. Nanofiltration with XLE membrane

In order to verify if the previous observed trends are valid for a different membrane, few experiments were carried out with ternary VFAs solutions and an XLE membrane.

3.2.1. Solutes retention in mixed solutions

The retentions of VFAs in ternary solutions (Ac:Pr:Bu = 33%:33%:33%) at three total concentrations (100, 200, and 250 mM) by

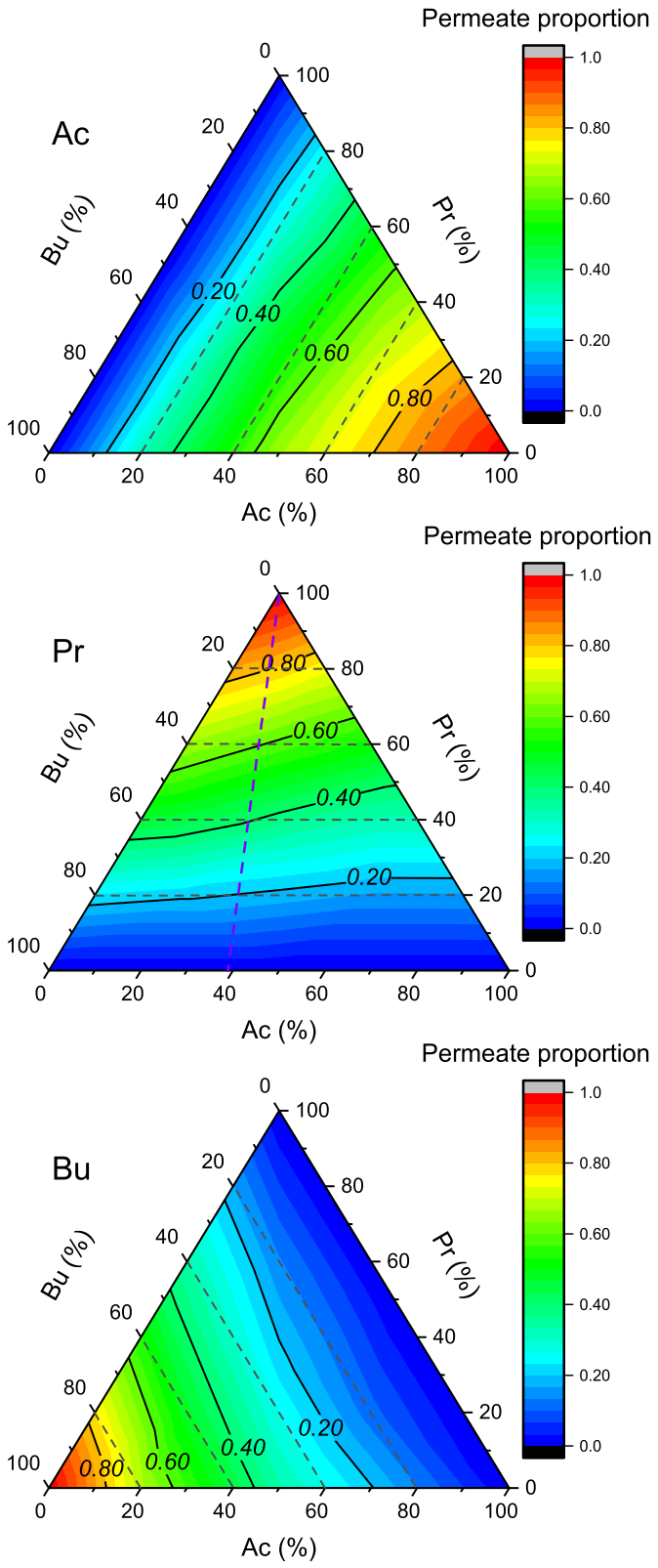

Fig. 9. VFAs proportions in the permeate (the plateau values, $P_i^{p^*}$) at all the compositions in the feed investigated, using NF-45 membrane. Data come from Table 4.

XLE membrane are given in Fig. 10 versus filtration flux. Filtration flux obtained at 500 mM was very low (results not shown).

Fig. 11 shows that the retentions of all the solutes are quite high, i.e. higher than 97% as soon as the filtration flux is higher than 0.25×10^{-5} m s^{-1}. No significant influence can be observed for the different total concentrations.

3.2.2. *Solute transfer*

The solutes proportions in the permeate versus filtration flux for VFAs ternary solutions (Ac:Pr:Bu = 33%:33%:33%) at various concentrations are given in Fig. 11a.

Despite the low solute concentration in the permeate, one can observe that the proportion of Ac in the permeate is higher than that in the feed, while the proportion of Bu observes the opposite trend. Plateau values at 43% and 27% for Ac and Bu are reached respectively, and no visible variation versus filtration flux is observed. Simultaneously, the proportion of Pr slightly decreases from 33% in the feed to 30% in the permeate.

Furthermore, it is shown that the filtration flux required for the permeate proportion to reach constant proportion (lower than 0.1×10^{-5} m s^{-1}) is much lower than that observed with NF-45 membrane (about 0.5×10^{-5} m s^{-1}).

The individual solutes flux versus total solute flux are shown in Fig. 11b.

As with NF 45 membrane, one can observe that the individual solutes flux increase linearly when the total solute flux increases. Again, no significant influence of the total concentration is pointed out.

Thus, the trends observed with XLE membrane are in agreement with those obtained with NF-45 membrane, despite the different membrane properties, like filtration flux and solute retention.

Otherwise, if we compare the results obtained with the 2 membranes for an identical feed proportion (Ac:Pr:Bu = 33%:33%:33%), one can notice that the solutes proportions in the permeate (plateau values) are not so different (Ac:Pr:Bu at 48%:31%:22% and 43%:30%:27%, for NF-45 and XLE membrane respectively). This deserves further investigation to determine whether or not the membrane properties influence the composition of the permeate or if it is mainly fixed according to the properties of the solutes.

4. Conclusion

The understanding of the mass transfer mechanism of complex solutions was pointed out as one of the most important prospects for the application of NF. Co-ions competition is usually mentioned to describe

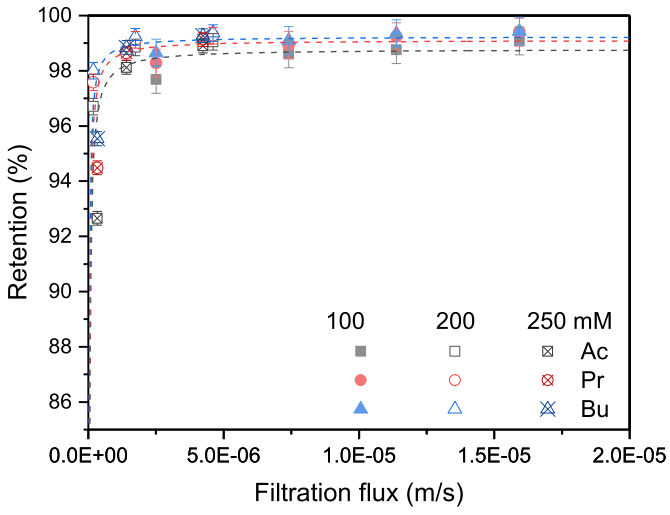

Fig. 10. Retention of VFAs in ternary solutions versus filtration flux (Ac:Pr:Bu = 33%:33%:33%) at various total concentrations, using XLE membrane.

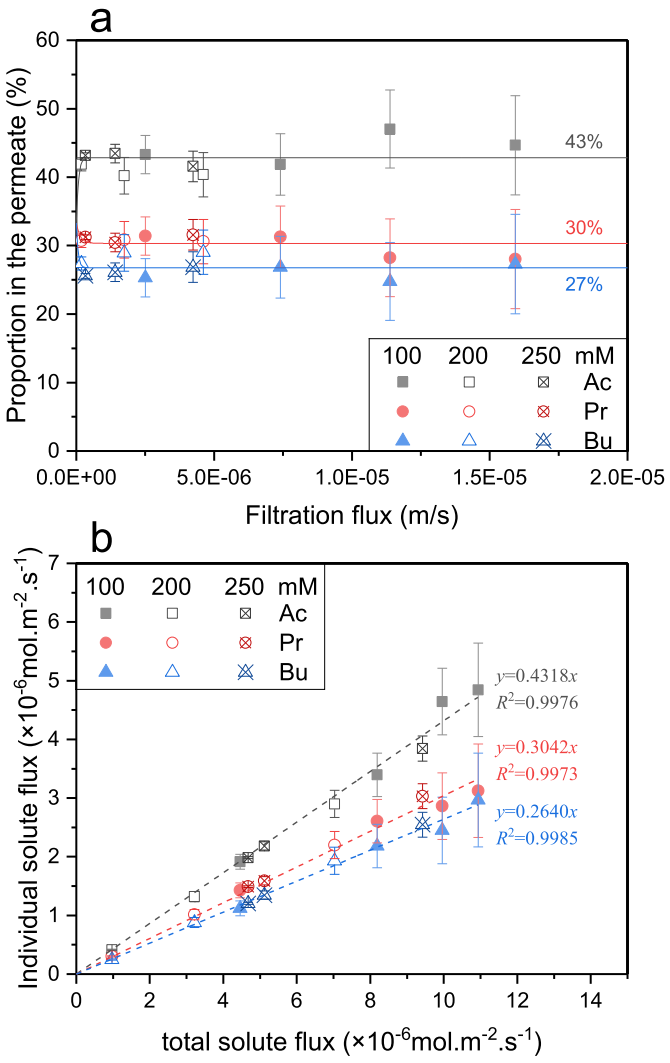

Fig. 11. (a) Solute proportion in the permeate versus filtration flux and (b) individual solute flux versus total solute flux for VFAs ternary solutions (Ac:Pr:Bu = 33%:33%:33%) at various concentrations using XLE membrane.

the difference of solute retentions between single and mixed solute solution. The general trend that was pointed out is a decrease of the less retained solute, frequently reported. Only few results were published showing an increase of the retention of the more retained solute. The influence of the solution concentration, as well as of the solutes proportion, on the individual solute retention was also reported.

In this work, an experimental study was carried out with solutions of different compositions containing VFAs and Cl and two nanofiltration membranes, NF 45 and XLE.

The results concerning the solutes retentions were first discussed. In agreement with previous studies, it was observed that the retention of the more retained solute increases compared to the one in a single solution, while that of the less retained one decreases. The difference between single and mixed solution depends on the solution composition (concentration and proportions of co-ions). For all the conditions investigated, it was observed that for a given filtration flux, the individual solutes retentions follow their molecular weight, i.e. $R_{Cl} < R_{Ac} < R_{Pr} < R_{Bu}$.

Then, the variation of the solutes proportions in the permeate versus filtration flux were investigated. It was found that for any feed composition, the proportion of any solute in the permeate reaches a plateau when the filtration flux is higher than a specific value. This plateau value does not depend on the total concentration but only on the solutes proportions in the feed.

Moreover, it was pointed out that the individual solute flux increases linearly with the total solute flux and does not depend on the total concentration but only on the VFAs proportions in the feed.

Same trends were pointed out with the two membranes investigated. It was observed that the solute proportions in the permeate obtained for a given feed proportions are not very different with the two membranes, despite their different characteristics in terms of mass transfer. This deserves further investigation to determine whether or not the membrane properties influences the composition of the permeate or if it is mainly fixed according to the properties of the solutes.

In this work, experiments were carried out at a constant stirring speed. It is thus difficult to conclude if concentration polarization can play a role. However, on one hand, results were compared at given filtration flux. On the other hand, it is known that the total concentration could also affect concentration polarization, and no influence of total concentration was observed on the permeate proportion. Nevertheless, further investigation with experiments at different stirring speed/cross-flow velocity would help to conclude about the possible influence of concentration polarization.

CRediT authorship contribution statement

Yin Zhu: Writing - review & editing. **Sylvain Galier:** Supervision, Writing - review & editing. **Hélène Roux-de Balmann:** Supervision, Writing - review & editing.

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Nomenclature

List of symbols

J	Filtration flux ($m \cdot s^{-1}$)
V	Volume (m^3)
S_m	Active surface of the membrane (m^2)
t	Time (s)
R	Retention (%)
c	Concentration ($mol \cdot m^{-3}$, abbreviate as mM)
P	Proportion of the solute (%)
A, B	Fitting parameters

Superscripts & subscripts

VFAs	Volatile Fatty Acids, i.e., Ac, Pr and Bu

mix	Mixed solution
sgl	Single solution
Ac	Acetate
Pr	Propionate
Bu	Butyrate
Cl	Chloride
f	Feed
p	Permeate
r	Retentate
m	Membrane
i	Individual solute
s	Total solutes

References

[1] B.M. Watson, C.D. Hornburg, Low-energy membrane nanofiltration for removal of color, organics and hardness from drinking-water supplies, Desalination 72 (1989) 11–22, https://doi.org/10.1016/0011-9164(89)80024-4.

[2] A. Lhassani, M. Rumeau, D. Benjelloun, M. Pontie, Selective demineralization of water by nanofiltration application to the defluorination of brackish water, Water Res. 35 (2001) 3260–3264, https://doi.org/10.1016/S0043-1354(01)00020-3.

[3] G.H. Chen, X.J. Chai, P.L. Yue, Y.L. Mi, Treatment of textile desizing wastewater by pilot scale nanofiltration membrane separation, J. Membr. Sci. 127 (1997) 93–99, https://doi.org/10.1016/S0376-7388(96)00311-0.

[4] B. Cuartas-Uribe, M.I. Alcaina-Miranda, E. Soriano-Costa, J.A. Mendoza-Roca, M. I. Iborra-Clar, J. Lora-Garcia, A study of the separation of lactose from whey ultrafiltration permeate using nanofiltration, Desalination 241 (2009) 244–255, https://doi.org/10.1016/j.desa1.2007.11.086.

[5] A. Bouchoux, H. Roux-de Balmann, F. Lutin, Investigation of nanofiltration as a purification step for lactic acid production processes based on conventional and bipolar electrodialysis operations, Separ. Purif. Technol. 52 (2006) 266–273, https://doi.org/10.1016/j.seppur.2006.05.011.

[6] J.G. Jacangelo, R.R. Trussell, M. Watson, Role of membrane technology in drinking water treatment in the United States, Desalination 113 (1997) 119–127, https://doi.org/10.1016/S0011-9164(97)00120-3.

[7] W.S. Lee, A.S.M. Chua, H.K. Yeoh, G.C. Ngoh, A review of the production and applications of waste-derived volatile fatty acids, Chem. Eng. J. 235 (2014) 83–99, https://doi.org/10.1016/j.cej.2013.09.002.

[8] M. Atasoy, I. Owusu-agyeman, E. Plaza, Z. Cetecioglu, Bio-based volatile fatty acid production and recovery from waste streams : current status and future challenges, Bioresour. Technol. 268 (2018) 773–786, https://doi.org/10.1016/j.biortech.2018.07.042.

[9] C.Y. Lin, C.H. Lay, A nutrient formulation for fermentative hydrogen production using anaerobic sewage sludge microflora, Int. J. Hydrogen Energy 30 (2005) 285–292, https://doi.org/10.1016/j.ijhydene.2004.03.002.

[10] C.C. Yarimtepe, N.A. Oz, O. Ince, Volatile fatty acid production dynamics during the acidification of pretreated olive mill wastewater, Bioresour. Technol. 241 (2017) 936–944, https://doi.org/10.1016/j.biortech.2017.05.173.

[11] H. Liu, P. Han, H. Liu, G. Zhou, B. Fu, Z. Zheng, Full-scale production of VFAs from sewage sludge by anaerobic alkaline fermentation to improve biological nutrients removal in domestic wastewater, Bioresour. Technol. 260 (2018) 105–114, https://doi.org/10.1016/j.biortech.2018.03.105.

[12] J. Schaep, B. der Bruggen, C. Vandecasteele, D. Wilms, Influence of ion size and charge in nanofiltration, Separ. Purif. Technol. 14 (1998) 155–162, https://doi.org/10.1016/S1383-5866(98)00070-7.

[13] D.X. Wang, M. Su, Z.Y. Yu, X.L. Wang, M. Ando, T. Shintani, Separation performance of a nanofiltration membrane influenced by species and concentration of ions, Desalination 175 (2005) 219–225, https://doi.org/10.1016/j.desal.2004.10.009.

[14] J.M.M. Peeters, J.P. Boom, M.H. V Mulder, H. Strathmann, Retention measurements of nanofiltration membranes with electrolyte solutions, J. Membr. Sci. 145 (1998) 199–209, https://doi.org/10.1016/S0376-7388(98)00079-9.

[15] J. Schaep, C. Vandecasteele, A.W. Mohammad, W.R. Bowen, Modelling the retention of ionic components for different nanofiltration membranes, Separ. Purif. Technol. 22–3 (2001) 169–179, https://doi.org/10.1016/S1383-5866(00)00163-5.

[16] J.M.K. Timmer, H.C. Vanderhost, T. Robbertsen, Transport of lactic acid through reverse-osmosis and nanofiltration membranes, J. Membr. Sci. 85 (1993) 205–216, https://doi.org/10.1016/0376-7388(93)85169-W.

[17] Z.V.R. Murthy, L.B. Chaudhari, Separation of binary heavy metals from aqueous solutions by nanofiltration and characterization of the membrane using Spiegler-Kedem model, Chem. Eng. J. 150 (2009) 181–187, https://doi.org/10.1016/j.cej.2008.12.023.

[18] M. Perry, C. Linder, Intermediate reverse osmosis ultrafiltration (RO UF) membranes for concentration and desalting of low molecular weight organic solutes, Desalination 71 (1989) 233–245, https://doi.org/10.1016/0011-9164(89)85026-X.

[19] S. Szoke, G. Patzay, L. Weiser, Characteristics of thin-film nanofiltration membranes at various pH-values, Desalination 151 (2002) 123–129, https://doi.org/10.1016/S0011-9164(02)00990-6.

[20] M.W. Vonk, J.A.M. Smit, Positive and negative ion retention curves of mixed electrolytes in reverse osmosis with a cellulose acetate membrane . An analysis on the basis of the generalized nernst-planck equation, J. Colloid Interface Sci. 96 (1983) 121–134.

[21] D.W. Nielsen, G. Jonsson, Bulk-phase criteria for negative ion rejection in nanofiltration of multicomponent salt solutions, Separ. Sci. Technol. 29 (1994) 1165–1182, https://doi.org/10.1080/01496399408005623.

[22] P. Khunnonkwao, K. Jantama, S. Kanchanatawee, S. Galier, H. Roux-de Balmann, A two steps membrane process for the recovery of succinic acid from fermentation broth, Separ. Purif. Technol. 207 (2018) 451–460, https://doi.org/10.1016/j.seppur.2018.06.056.

[23] S.H. Kang, Y.K. Chang, Removal of organic acid salts from simulated fermentation broth containing succinate by nanofiltration, J. Membr. Sci. 246 (2005) 49–57, https://doi.org/10.1016/j.memsci.2004.08.014.

[24] A.E. Yaroshchuk, Negative rejection of ions in pressure-driven membrane processes, Adv. Colloid Interface Sci. 139 (2008) 150–173, https://doi.org/10.1016/j.cis.2008.01.004.

[25] B. Van der Bruggen, J. Schaep, W. Maes, D. Wilms, C. Vandecasteele, Nanofiltration as a treatment method for the removal of pesticides from ground waters, Desalination 117 (1998) 139–147, https://doi.org/10.1016/S0011-9164(98)00081-2.

[26] P. Somasundaran (Ed.), Encyclopedia of Surface and Colloid Science, second ed., CRC Press, New York, 2006.

[27] B. Balannec, M. Vourch, M. Rabiller-Baudry, B. Chaufer, Comparative study of different nanofiltration and reverse osmosis membranes for dairy effluent treatment by dead-end filtration, Separ. Purif. Technol. 42 (2005) 195–200, https://doi.org/10.1016/j.seppur.2004.07.013.

[28] S.N. Diop, M.A. Diallo, C.K. Diawara, D. Cot, Intrinsic properties and performances of NF270 and XLE membranes for water filtration, WATER Sci. Technol. SUPPLY. 11 (2011) 186–193, https://doi.org/10.2166/ws.2011.024.

[29] P. Xu, J.E. Drewes, T.U. Kim, C. Bellona, G. Amy, Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications, J. Membr. Sci. 279 (2006) 165–175, https://doi.org/10.1016/j.memsci.2005.12.001.

[30] A. Bouchoux, H. Roux-de Balmann, F. Lutin, Nanofiltration of glucose and sodium lactate solutions: variations of retention between single- and mixed-solute solutions, J. Membr. Sci. 258 (2005) 123–132, https://doi.org/10.1016/j.memsci.2005.03.002.

[31] M. Nilsson, G. Trägårdh, K. Östergren, The influence of pH, salt and temperature on nanofiltration performance, J. Membr. Sci. 312 (2008) 97–106, https://doi.org/10.1016/j.memsci.2007.12.059.

[32] C. Umpuch, S. Galier, S. Kanchanatawee, H. Roux-de Balmann, Nanofiltration as a purification step in production process of organic acids: selectivity improvement by addition of an inorganic salt, Process Biochem. 45 (2010) 1763–1768, https://doi.org/10.1016/j.procbio.2010.01.015.

[33] J. Luo, Y. Wan, Effects of pH and salt on nanofiltration-a critical review, J. Membr. Sci. 438 (2013) 18–28, https://doi.org/10.1016/j.memsci.2013.03.029.

[34] S.I. Li, C. Li, Y.S. Liu, X.L. Wang, Z.A. Cao, Separation of (L)-glutamine from fermentation broth by nanofiltration, J. Membr. Sci. 222 (2003) 191–201, https://doi.org/10.1016/S0376-7388(03)00290-4.

[35] M. Su, D.X. Wang, X.L. Wang, M. Ando, T. Shintani, Rejection of ions by NF membranes for binary electrolyte solutions of NaCl, NaNO3, CaCl2 and Ca(NO3)2, Desalination 191 (2006) 303–308, https://doi.org/10.1016/j.desal.2005.06.041.